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Confirming the existence of π-allyl-palladium intermediates during the reaction of *meta* photocycloadducts with palladium(II) compounds†

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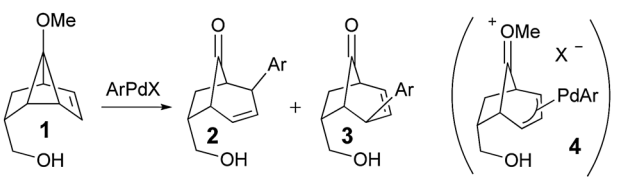
The transient existence of π-allyl-palladium intermediates formed by the reaction of $Pd(OAc)_2$ and anisole-derived *meta* photocycloadducts has been demonstrated using NMR techniques. The intermediates tended to be short-lived and underwent rapid reductive elimination of palladium metal to form allylic acetates, however this degradation process could be delayed by changing the reaction solvent from acetonitrile to chloroform.

The role of π-allyl-palladium intermediates in synthetic organic chemistry has attracted a great deal of interest in laboratories worldwide. They play a major part in the Tsuji–Trost reaction[1] for which the stereochemical outcome of the reaction is controlled by the ligand.[2] Other methods of generating π-allyl-palladium intermediates have involved the addition of aryl palladium halides to 1,3-dienes[3,4] or allenes.[5,6] The latter examples have provided the opportunity to assemble the vinyl cyclopropane functionality in the case when an anion is generated two carbon atoms away from the π-allyl-palladium moiety.[5,6] Aside from this example there is a powerful connection between organopalladium chemistry and vinyl cyclopropane systems in that the former can be used to assemble or disassemble the latter. Vinyl cyclopropane systems have also been prepared using palladium-mediated domino polycyclization reactions,[7] when the release of palladium from an intermediate required the formation of a three-membered ring before β-hydride elimination could occur. Likewise the olefinic-character of cyclopropane bonds has been employed to generate π-allyl-palladium intermediates[8] from vinyl cyclopropane systems using a chloropalladation process and the mechanism of the ring-opening stage has been shown to be dependent on the reaction conditions used.[9] We have previously speculated[10,11] on the transient existence of π-allyl-palladium intermediates by the interaction of palladium(II) compounds with the vinyl cyclopropane portion of certain *meta* photocycloadducts and this communication provides evidence to support this mechanistic proposition.

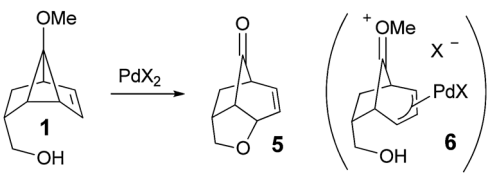
Whilst investigating electrophile-induced addition/fragmentation reactions of *meta* photocycloadducts, we discovered that the two regioisomeric arylation products **2** and **3** were formed when the anisole/allyl alcohol-derived *meta* photocycloadduct **1** was subjected to Heck-type arylation conditions.[10] This led us to speculate that an intermediary π-allyl-palladium species similar to **4** was being generated during the transformation (Scheme 1).

Further investigation of the palladium-promoted chemistry of **1** revealed that it could be oxidatively cyclised to the tricycle **5** in the presence of a palladium(II) salt and again a π-allyl-palladium intermediate (**6**) was proposed to account for the transformation (Scheme 2).[11]

In order to confirm the existence of a π-allyl-palladium intermediate during the reaction of a *meta* photoadduct with a palladium(II) salt, a model system was chosen so that it could be easily prepared and any chemical changes readily monitored using NMR spectroscopy. It was also important that the model substrate did not contain an internal nucleophile and thereby avoid intramolecular substitution reactions (see formation of **5** from **1**). Hence the *exo* and *endo* photoadducts **9**[10b] and **10**[10b,c]



Scheme 1 Pd(II) mediated arylation of **1**.



Scheme 2 Pd(II) mediated oxidation of **1**.

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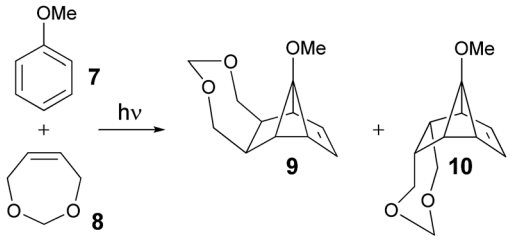
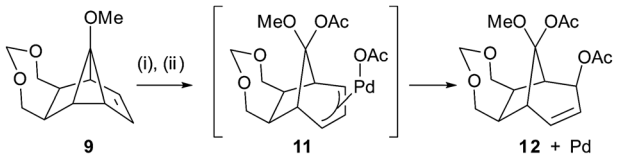


Scheme 3 Formation of photoadducts **9**[10b] and **10**.[10b,c]



Scheme 4 Conversion of *meta* photoadduct **9** to **12** *via* π-allyl-palladium intermediate **11**.

were used, which were derived from *meta* photocycloaddition[12] of anisole **7** and *cis*-4,7-dihydro-1,3-dioxepin **8** (Scheme 3).

We began our search to identify a π-allyl-palladium intermediate using the *exo* adduct **9** and palladium(II) dichloride as the source of palladium. A 1 : 1 mixture of these two components was prepared in a deuterated solvent ($CDCl_3$, DMF-d_7 or MeCN-d_3) so that the progress of the reaction could be monitored by ^{1}H NMR spectroscopy, however no spectral change from that of the starting *exo* adduct **9** was observed during these preliminary experiments. Hence the palladium source was changed to palladium(II) diacetate. A 1 : 1.1 mixture of the *exo* adduct **9** and $Pd(OAc)_2$ was dissolved in MeCN-d_3 and then added to an NMR tube. At frequent intervals after combining the solvent and reagents ^{1}H NMR spectra were run so that any chemical changes taking place could be monitored. Our initial conclusion was that all of **9** had been consumed very quickly to give principally two new compounds with one apparently undergoing rapid conversion to the other. Visibly it was obvious that chemical changes were occurring, because the initially orange solution became an increasingly darker brown colour and a fine black precipitate of palladium metal coated the internal surface of the NMR tube. After 2 hours the reaction mixture was concentrated and the residue was subjected to column chromatography to afford the bis-acetate product **12** as a crystalline solid in 30% yield (Fig. 1).†

When this experiment was originally conducted, there had only been a limited supply of MeCN-d_3 available in the laboratory and this caused us to repeat the reaction using non-deuterated acetonitrile as the initial reaction solvent. In order to monitor the reaction using NMR spectroscopy the acetonitrile was removed *in vacuo* after 4 min and replaced with $CDCl_3$. The reaction mixture was immediately analysed using NMR spectroscopy, which confirmed the existence of the π-allyl-palladium intermediate **11**. We also found that this solvent replacement process of exchanging acetonitrile by $CDCl_3$ had the unexpected advantage of slowing down the rate of reductive elimination of palladium from **11** to give **12**, which allowed a valuable time-window of opportunity to characterise **11**. These results are summarized in Scheme 4.

A related series of experiments were undertaken using the *endo* photoadduct **10** and $Pd(OAc)_2$ initially being dissolved in acetonitrile, concentrated and re-solvated in $CDCl_3$. Again we were able to observe the π-allyl-palladium intermediate **13**, which over time degraded to the bis-acetate product **14** by reductive elimination of palladium metal onto the internal surface of the NMR tube (Scheme 5).

A comparison of the ^{1}H and the ^{13}C NMR spectra for compounds **11** and **13** (with certain key signals highlighted) are presented in Fig. 2 and 3 respectively. The ^{1}H and ^{13}C NMR spectra† of **11** and **13** each revealed the presence of only two acetate signals, which indicated that their formation from **9** and **10** respectively were stereoselective processes. From the X-ray diagram of **12** (Fig. 1) we inferred that the stereochemistries of the methoxy-acetate acetal moieties of **11** and **13** were as shown (Schemes 4 and 5). The symmetrical nature of the π-allyl-palladium moieties of **11** and **13** was demonstrated by the doubling-up of certain signals within their ^{1}H and ^{13}C NMR spectra. Hence, although both had molecular formulae of $C_{16}H_{22}O_7Pd$, only 12 peaks in their respective ^{13}C NMR spectra could be attributed to **11** or **13**, which indicated that each structure exhibited a plane of symmetry.

In addition to the results described above the reactions of *endo* or *exo* photoadducts **9** or **10** with $Pd(OAc)_2$ complexed to various ligands (PPh_3, BINAP or sparteine) were also investigated, however no chemical changes to the photoadducts were observed upon addition to the palladium complexes.

We have shown that the alkenyl cyclopropane moiety of a *meta* photocycloadduct would react with $Pd(OAc)_2$ to form a π-allyl-palladium intermediate. This intermediate was short-lived and, in the absence of an internal nucleophile, underwent reductive elimination of palladium to afford an allylic acetate species. It was discovered that this latter process could be

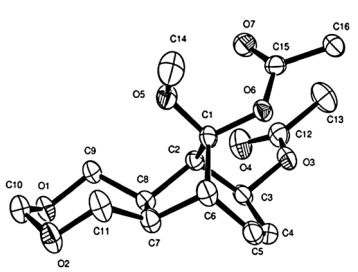
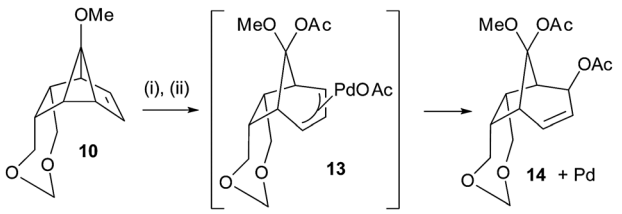


Fig. 1 ORTEP diagram of compound **12**.



Scheme 5 Conversion of *meta* photoadduct **10** to **14** *via* π-allyl-palladium intermediate **13**.

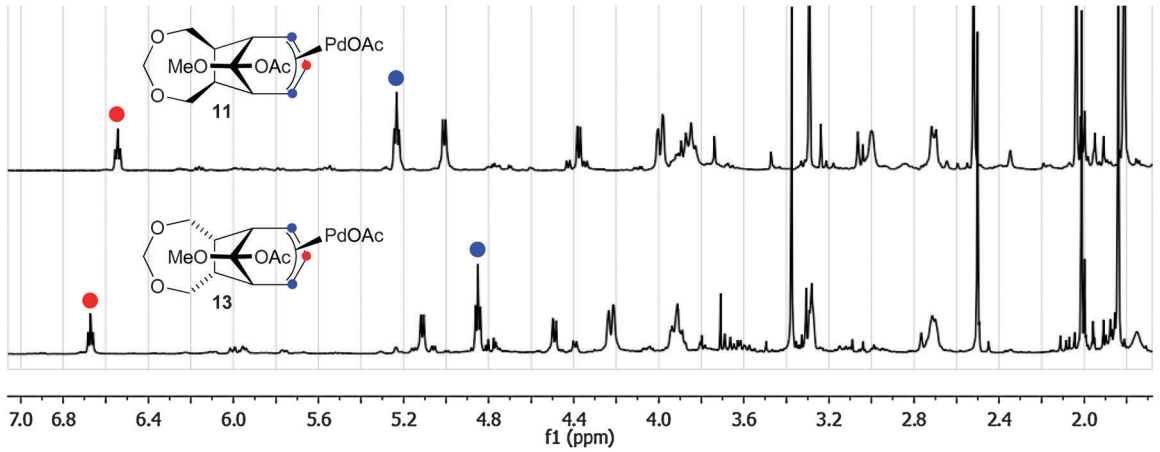


Fig. 2 Comparison of ^{1}H NMR spectra for the π-allyl-palladium intermediates **11** and **13**. (The colour-coded signals arising from the π-allyl-palladium moiety are highlighted in the spectra.)

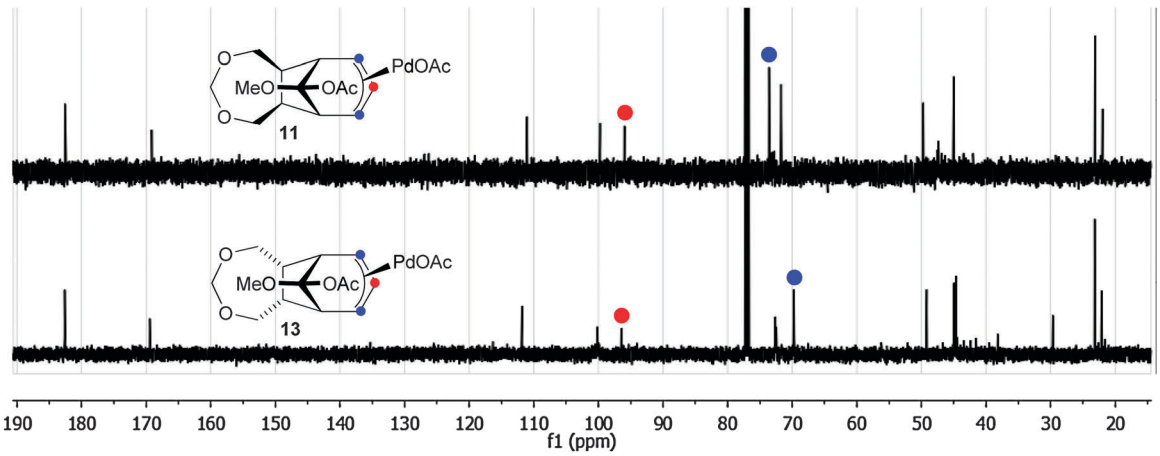


Fig. 3 Comparison of ^{13}C NMR spectra for the π-allyl-palladium intermediates **11** and **13**.[13] (The colour-coded signals arising from the π-allyl-palladium moiety are highlighted in the spectra.)

delayed by changing the reaction solvent from acetonitrile to chloroform.

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